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The Analysis of Aluminum-Copper Alloys

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THE ANALYSIS OF ALUMINUM-COPPER ALLOYS

BY

SCOTT CHAMPLIN TAYLOR

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

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June 3, 1913.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Scott Champlin Taylor

ENTITLED The Analysis of Aluminum-Copper Alloys

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

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THE ANALYSIS OF ALUMINUM-COPPER ALLOYS.

Introduction.

The extensive manufacture of automobiles, motor-cycles, and airships has created a demand for materials which are strong and light and will satisfy the varied requirements in vehicles of these types.

Many kinds of special steels and other alloys have been tried for these purposes and at the present time a large number of alloys are used in the construction of a single vehicle. The special steels generally meet the requirement of strength but not that of lightness. There is, however, an exception to the latter in the case of a few steels which have an unusually great tensile strength. In these cases a given weight of steel will give a greater strength than an equal weight of an aluminum alloy.

The requirement of lightness has been met largely by alloys of aluminum with various metals which are intended to increase the strength without materially increasing the weight of the alloys.

Perhaps the best success has been attained by the addition of copper and this fact has resulted in a very careful study of aluminum-copper alloys.[1] A range of from two to four percent of copper has been found most successful for commercial purposes and especially is this true of the alloys containing six to eight percent copper. According to H. H. Gillett[2] ninety percent of all cast aluminum contains about eight percent copper and ninety-two percent aluminum.

The extensive use of this alloy has rendered necessary a careful analytical control and has suggested the advisability of detailed study of the methods used in its analyis. With this in view the Velie Motor Vehicle Company of Moline, Illinois sent samples of the same aluminum-copper alloy to a number of universities for comparative analyses. Commenting on the results reported, Mr. C. B. Rose, chief engineer of the company writes as follows, under the date of July 6, 1912. "There seems to be a very great discrepancy among the different chemists in the analyses of the alloy. In fact we can find no two chemists who agree. . . . . . All of these analyses are by universities with the exception of one which is by our own chemist."

The following are the results as reported by the various analysts.

1. Professor F. S. Kedzie of the Michigan Agricultural College reported the following constituents:

Copper	6.14 %
Aluminum	92.1 %
	92.3 %

The remaining small percent silicon.

He describes further several careful, special tests which he has made for zinc and states that in his opinion no zinc is present, but if it is present it cannot exist in a largeramount than 0.76 %.

2. The following results were reported by J. M. Lindgren, chemist of the Illinois Geological Survey:

Copper	6.42 %
Aluminum	92.19 %
Iron	0.11 %

Silicon	0.52 %
Zinc	0.56 %
Lead	0.13 %

3. An analysis from an important Western university, the name of which was not given, shows the following:

Aluminum	89.50 %
Copper	9.32 %
Iron	0.62 %
Zinc	0.48 %
Silicon	trace

Other analyses were as follows:

4.

Aluminum	91.85 %
Copper	6.14 %
Silica	1.25 %

No zinc present.

5.

Aluminum	89.25 %
Copper	7.40 %
Zinc	3.10 %
Iron	0.30 %

As may be seen the main differences are in the percentages of copper, aluminum and zinc reported; while analysis number 4 shows no zinc at all. That this is a point of considerable importance is shown in a letter from Mr. Rose dated February 28, 1912. He states that the reason the company was having this alloy analyzed was because they believed it contained zinc.

Professor S. W. Parr in a letter of July 12, 1913, in regard to the discrepancies in the chemical results on the aluminum alloys

says: first, "There is considerable tendency on the part of such mixtures to segregate in casting, so that comparative results to have real value should be taken from the same piece in finely divided condition, and thoroughly mixed before dividing and distributing." second, "There are a few analytical difficulties involved in the separation of zinc and aluminum under any proportions, but these are accentuated when the percentage of aluminum is high and that of zinc low."

There are thus two possible sources for these discrepancies. Firstly, a difference in the composition of the different sections due to segregation and secondly, the incomplete separation of the aluminum from the other constituents.

Purpose Of Present Work.

In order to investigate the above discrepancies and to find out the methods which are best adapted to the accurate analysis of such alloys, the present investigation was undertaken. It was desired to show first, the correct results on the above sample of alloy, especially the proper percentages of aluminum and copper and the presence or absence of zinc. Second,to demonstrate whether the discrepancies in the results of the different analysts were due (1), to segregation and resulting differences of the samples submitted or (2) to errors in the analytical separation.

In this work three different pieces of alloy were analyzed.

1. The sample (to be designated by "X") analyzed by J. M. Lindgren and reported as shown on page two.
2. The original casting (to be designated by "Y") from which all of the samples sent to the various analysts, were taken. This was furnished upon special request by the Velie Motor Vehicle Company.
3. A similar casting (the different sections of which were designated by "B", "C", "E") also furnished by the above company, from which three sections were taken for comparative analysis and study of structure and segregation.

EXPERIMENTAL.

The Separation of Constituents.

In the analysis of any alloy the first thing to be considered is a method for the separation of the different constituents. The main difficulty encountered where large percentages of aluminum are present seems to be due to the occlusion of the other constituents by the gelatinous precipitate of aluminum hydroxide. It was thought that this could be overcome by dissolving the precipitate and reprecipitating the aluminum. Here, however, another difficulty was encountered, stated as follows by Treadwell and Hall[3]: "The freshly precipitated aluminum hydroxide $Al(OH)_3$ is readily soluble in dilute acids; but after standing some time under water or after long boiling it becomes more difficultly soluble, so that it is necessary to digest it with acid for a long time in order to bring it completely into solution. The hydrate $Al(OH)_3$ is probably changed into $Al_2O(OH)_4$ or $AlO(OH)$ which are much more insoluble."

By this reprecipitation therefore, the occlusion of other elements may be avoided, but the large amount of acid and the continued boiling required to dissolve the precipitate will prevent the precipitation of zinc so that it is necessary that some other method be devised, in case the latter is to be determined. Bearing these things in mind it seemed better to separate the different constituents in such a manner as to leave the aluminum in solution.

Of the methods recommended by various authors for the separation of mixtures containing copper, zinc and aluminum, two, the barium carbonate[4] and the acetate[5] methods were found to be open to the above

objections.

Two methods were therefore tried which left the aluminum in solution and precipitated the other elements.

First, The Modified Waring Method.[6] This depends upon the fact that a strip of aluminum will precipitate the copper quantitatively from a solution, acid with sulphuric acid. The precipitated copper is filtered off and the solution neutralized with sodium carbonate, then made slightly acid with a weak acid and the zinc precipitated with hydrogen sulphide. The aluminum must be determined in a separate sample.

Second, The copper was first removed from acid solution with hydrogen sulphide, the precipitate filtered off and the filtrate evaporated to dryness several times to free it from the excess acid. The residue was then taken up with water and the zinc precipitated as zinc sulphide.

Both of these methods seemed equally successful.

Methods of Determining the Different Constituents.

Zinc.

After the copper has been entirely precipitated, by means of hydrogen sulphide or a strip of aluminum, and filtered off, the filtrate is neutralized with sodium bicarbonate and then made acid with twenty percent formic acid, adding six cubic centimeters excess acid. Hydrogen sulphide was next led into the solution which should have precipitated the zinc as zinc sulphide if it were present. This precipitate was dissolved in nitric acid and the solution neutralized with ammonium hydroxide using litmus solution as the indicator. To this solution was added diammonium hydrogen phosphate. The precipitate was filtered, washed, ignited and weighed as $Zn_2P_2O_7$. The precautions to be observed in this determination are, (1) to have the solution just neutral, as the precipitate is soluble in both acids and alkalies, (2) care should be exercised that the precipitating agent (diammonium hydrogen phosphate) is free from other phosphates. This freedom may be obtained by adding to a solution of the diammonium hydrogen phosphate, commonly obtained, dilute ammonium hydroxide until the solution just becomes pink with phenol-phthalein as the indicator. It was thought at the beginning of this work that this alloy contained a small percentage of zinc but as far as these investigations have shown, no satisfactory results for zinc where found. Nevertheless the methods studied have shown that they would be equally applicable to alloys which contain small percentages of zinc.

Copper.

The copper was determined electrolytically. It was thought

at first that it would be possible to determine the copper in the presence of aluminum but the results so obtained were quite unsatisfactory. This was due to the large excess of acid required and resulted in a spongy deposit of copper. The copper was therefore first separated by precipitation by either hydrogen sulphide or aluminum.

The best deposit was obtained in a solution containing five percent sulphuric and nitric acids and using a low current density. A current of 0.15 to 0.40 amperes was found to be the most satisfactory for a good deposit. The use of such a low amperage required a long time for the complete deposition of the copper so a current of one ampere was tried. The first part of the deposit seemed to be very firmly attached to the electrode but after all of the copper was deposited and the electrode was washed a large amount of the copper fell off.

Great care should be taken in washing the electrode after the deposition is complete. The best procedure in order that the copper will not be dissolved by the acid present is to open the lower stop-cock and pour distilled water into the top of the vessel as fast as the colution flows out of the bottom. This is continued until the current falls off completely which shows that the acid has been entirely removed. As long as the current is flowing the copper will not be dissolved. After the deposit has been thoroughly washed in this manner it is quickly dried, care being taken to prevent oxidation since freshly precipitated copper is readily acted upon by the oxygen of the air.

The deposits obtained were very uniform, bright and adherent.

The following percentages of copper were obtained on the original piece of alloy.

1. 6.50 % "X"

2. 6.48 % "$Y"_1$

6.46 % "$Y"_2$

6.67 % "$Y"_3$

6.84 % "X" (slightly oxidized)

The above results check within experimental error, the difference from the mean being about 0.1 %. This shows that the percentage of copper is the same throughout the casting and that the discrepancies are due to incomplete separation of the constituents and not to segregation. These percentages check with those obtained by J. M. Lindgren, page two.

The following percentages were obtained on another piece which was being prepared for etching:

6.17 % "C"

6.14 % "B"

6.08 % "E"

Aluminum

The aluminum was determined on a 0.2 gram sample in the usual manner of precipitation as the hydroxide and weighing as the oxide. There were two variations followed which seemed equally efficient. In the first of these the aluminum precipitate was highly colored with the deep blue of the copper salt. To remove this the aluminum hydroxide was dissolved in boiling nitric acid and the aluminum reprecipitated. The other procedure was to remove the copper by means of hydrogen sulphide in acid solution, then to precipitate the aluminum in the usual manner.

The following average percentages of aluminum were obtained on the original piece of alloy:

92.46 % "X"

91.82 % "$Y"_1$

91.69 % "Y_2"

91.92 % "Y_3"

These results are not as uniform as those obtained for copper; but in view of the difficulties attending the determination of large amounts of aluminum, the agreement is not bad and is within the limits of reasonable experimental error. The fact that the results checked with those obtained by J. M. Lindgren (page two) should be noted. The results show that the discrepancies are due to incomplete separation of the different constituents and not to segregation.

The following percentages were obtained on another piece which was being prepared for etching:

89.78 % "E"

89.93 % "D"

89.72 % "C"

Silicon.

The alloy was dissolved in hydrochloric acid, evaporated to dryness and baked. The residue was taken up with hydrochloric acid and the process repeated. This residue was then taken up with concentrated hydrochloric acid and digested for half an hour. An equal volume of water was added and then filtered. This process rendered all the silicon insoluble. The residue was then ignited and weighed. This residue was impure silica. It was purified by adding sulphuric acid and hydrofluoric acid and evaporated to dryness. The loss in weight gave the pure silica.

The following percentages of silicon were obtained on the original piece of alloy:

0.44 % "X"

0.45 % "Y_1"

0.43 % "Y_2"

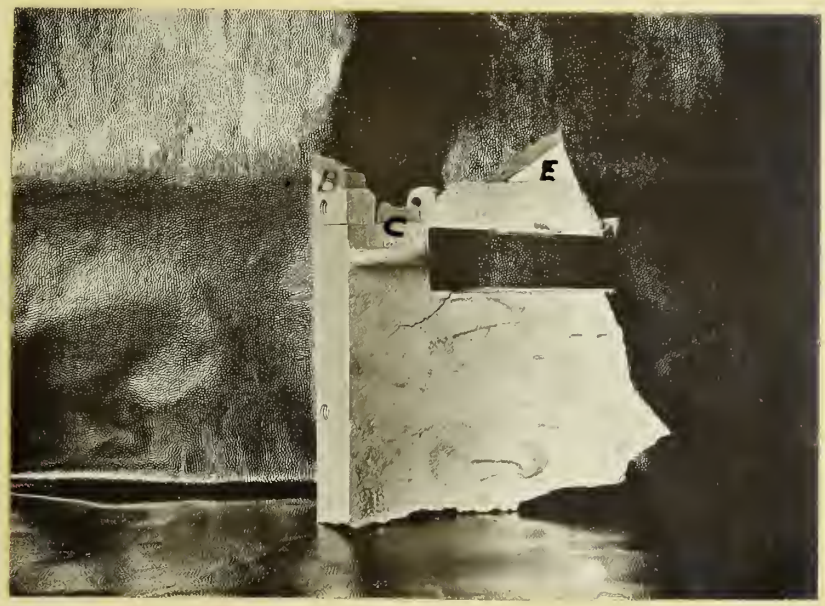
0.42 % "Y_3"

The uniformity of all results obtained on the same sample and the fact that they closely agreed with those obtained by J. M. Lindgren show that the methods used are capable of giving accurate results and that the alloy is of a uniform composition.

Study of Micro-structure.

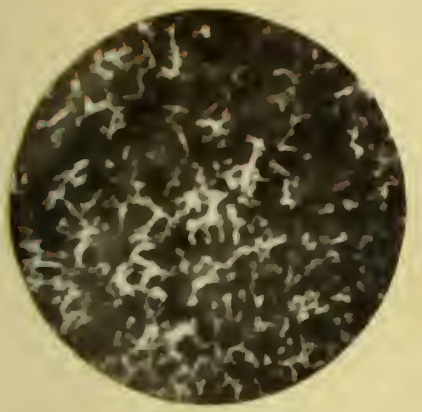
To verify the results obtained analytically in regard to uniformity of composition, a study of the structure and segregation was undertaken.

Three sections (samples "B", "C", and "E", page 5) were taken from a casting submitted by the Velie Company. The position of these sections are shown in the accompanying photograph.

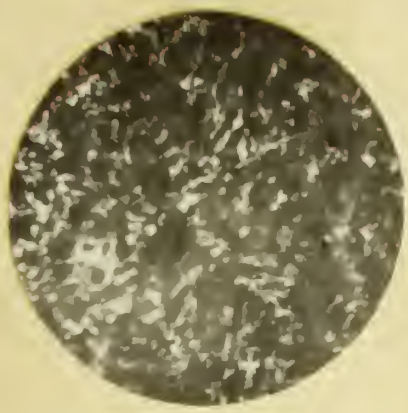


Section "B" was taken from a thick portion of the casting, Section "C" was taken from a thin portion but was surrounded by heavy parts. Section "E" was taken from a thin section, which should have cooled very rapidly when the metal was cast. These sections were ground and polished on a rouge surface, etched in seven percent hydrochloric acid for three minutes. They were then thoroughly washed, dried, and photographed.

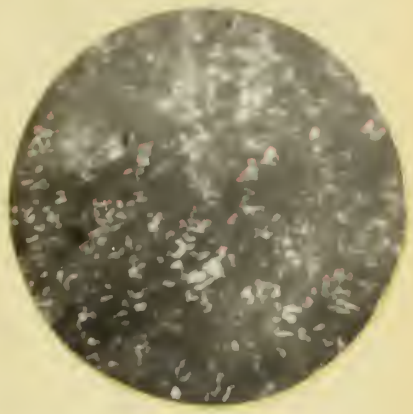
The photographs of the different sections are shown as follows:



Section "B" X 100



Section "C" X 100



Section "E" X 100

These photographs are practically uniform in structure, the slight difference in grain structure is due to a difference in the rate of cooling which may be ascribed to the difference in thickness above noted. This uniformity shows that segregation has not taken place in the casting under investigation.

CONCLUSION.

As was pointed out in the introduction on page four, the purpose of this work was to show whether the discrepancies in the analytical results obtained by the different analysts were due to , (1) a difference in the composition due to segregation, or (2) to the incomplete separation of the aluminum from the other constituents.

The results obtained show conclusively that the second conclusion is the right one. Both the chemical composition and micro-structure are uniform throughout and no evidence of segregation has been found.

The work has shown that special care must be exercised in obtaining complete separation of the constituents in alloys of this type and accurate and concordant results can only be obtained by careful standardization of methods used.

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2. Original Communications of the Eighth International Congress of Applied Chemistry, Volume II, pages 105-112. "The Influence of Pouring Temperature on Aluminum Alloys." by H. H. Gillett.

3. Treadwell and Hall, Qualitative Analysis, Volume I, page 71.

4. Treadwell and Hall, Quantitative Analysis, Volume II, pages 134-136.

5. Treadwell and Hall, Quantitative Analysis, Volume II, pages 136-137.

6. Quantitative Analysis for Engineers - Miller, pages 77-79.

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